

CLAIMS

1. Solid polymer electrolyte, characterized in that it comprises at least one methacrylonitrile polymer chosen from:

- linear homopolymers of high mass, which may or may not be reinforced;
- homopolymers, which may or may not be reinforced, rendered three-dimensional by crosslinking;
- linear methacrylonitrile copolymers of high mass;
- copolymers of methacrylonitrile and of at least one comonomer which makes possible crosslinking, which copolymers are rendered three-dimensional by crosslinking.

2. Solid polymer electrolyte according to Claim 1, characterized in that the methacrylonitrile polymer is a copolymer of methacrylonitrile and of a comonomer which makes possible the use of solvents with low boiling points and/or of a comonomer which makes possible internal plasticization of the polymer by decreasing its glass transition temperature and/or of a comonomer which makes possible the introduction of the ionic functional group in order to obtain a unipolar electrolyte.

3. Solid polymer electrolyte according to Claim 1, characterized in that it comprises a methacrylonitrile homopolymer and from 5% to 20% by mass of silica.

4. Solid polymer electrolyte according to <sup>claim 1</sup> ~~either~~ of Claims 1 and 2, characterized in that the methacrylonitrile polymer is a copolymer of methacrylonitrile and of at least one acrylic or methacrylic comonomer.

5. Solid polymer electrolyte according to Claim 4, characterized in that the methacrylonitrile polymer is a copolymer of methacrylonitrile and of at least one acrylic comonomer corresponding to the formula  $\text{CHX}=\text{CZ}-\text{CO}-\text{V}-\text{Y}$ , in which:

- X represents  $\text{C}_n\text{H}_{2n+1}$ , with  $0 \leq n \leq 8$ ;

- Z represents  $C_nH_{2n+1}$ , with  $0 \leq n \leq 8$ , or  $(CH_2)_mCN$ , with  $0 \leq m \leq 4$ ;

- V represents O, NH or NR, R represents  $C_nH_{2n+1}$ , with  $0 \leq n \leq 8$ ;

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Y represents a  $C_nH_{2n+1}$  radical, with  $0 \leq n \leq 8$ , a radical carrying an oxirane group  $C_nH_{2n}-(CH-CH_2)-O$ , with  $1 \leq n \leq 4$ , or a radical  $[(CH_2)_m-O]_pR'$ , in which  $m = 2, 3$  or  $4$ ,  $1 \leq p \leq 50$  and  $R'$  represents  $C_nH_{2n+1}$ , with  $0 \leq n \leq 8$ .

10 6. Solid polymer electrolyte according to Claim 1, characterized in that the methacrylonitrile polymer is a copolymer of methacrylonitrile and of an alkylenebisacrylamide corresponding to the formula  $CH_2=CH-CO-NH-(CH_2)_n-NH-CO-CH=CH_2$  in which  $0 \leq n \leq 6$ ,

15 7. Solid polymer electrolyte according to Claim 1, characterized in that the methacrylonitrile polymer is a copolymer of methacrylonitrile and of an alkyl diacrylate or dimethacrylate or of poly(ethylene glycol) diacrylate or dimethacrylate.

20 8. Solid polymer electrolyte according to Claim 5, characterized in that the comonomer is a poly(ethylene glycol) *methylether* ~~methoxy~~ methacrylate  $CH_2=C(CH_3)-COO-(CH_2)_2-O-]_pCH_3$  with  $1 \leq p \leq 50$ .

25 9. Solid polymer electrolyte according to Claim 5, characterized in that the comonomer is a hydroxyalkyl acrylate corresponding to the formula  $CH_2=CH-CO-O-(CH_2)_m-OH$  with  $1 \leq m \leq 8$  or a hydroxyalkyl methacrylate corresponding to the formula  $CH_2=C(CH_3)-CO-O-(CH_2)_m-OH$  with  $1 \leq m \leq 8$ .

30 10. Solid polymer electrolyte according to Claim 9, characterized in that the comonomer is chosen from hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxybutyl acrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate and hydroxybutyl  
35 methacrylate.

*(11)* Solid polymer electrolyte according to Claim 1, characterized in that the methacrylonitrile polymer is a terpolymer of methacrylonitrile (MAN), of poly(ethylene glycol) *methylether* ~~methoxy~~ methacrylate (PEGMM) and

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of hydroxyethyl methacrylate (HEMA) in the respective molar proportions x, y and z such that  $40\% < x < 97\%$ ,  $1\% < y < 40\%$  and  $1\% < z < 20\%$ .

12. Solid polymer electrolyte according to Claim 1, characterized in that the methacrylonitrile polymer is a terpolymer of methacrylonitrile (MAN), of octyl methacrylate or of hexyl acrylate, and of hydroxyethyl methacrylate (HEMA) in the respective molar proportions x, y and z such that  $60\% < x < 97\%$ ,  $1\% < y < 30\%$  and  $1\% < z < 15\%$ .

13. Solid polymer electrolyte according to Claim 1, characterized in that the methacrylonitrile polymer is a terpolymer of methacrylonitrile (MAN), of butyl methacrylate and of hydroxyethyl methacrylate (HEMA) in the respective [lacuna] proportions x, y and z such that  $50\% < x < 97\%$ ,  $1\% < y < 40\%$  and  $1\% < z < 15\%$ .

14. Solid polymer electrolyte according to Claim 2, characterized in that the methacrylonitrile polymer is a bipolymer of methacrylonitrile and of a monomer carrying a carboxylate, phosphate, phosphonate, sulfonate or perfluorosulfonate ionic functional group.

15. Solid polymer electrolyte according to Claim 14, characterized in that the monomer carrying an ionic functional group is lithium N,N-diallyl-1-amidotetrafluoroethanesulfonate  $(CH_2=CH-CH_2)_2NCO-CF(CF_3)SO_3Li$  or lithium allyloxyltetrafluoroethyl-sulfonate  $CH_2=CH-CH_2-O-(CF_2)_2-SO_3Li$ .

16. Solid polymer electrolyte according to Claim 4, characterized in that the comonomer is glycidyl acrylate or glycidyl methacrylate.

17. Solid polymer electrolyte according to Claim 4, characterized in that the comonomer is an ~~isocyanate~~ <sup>methacryloyl isocyanate</sup> acryloyl or methacryloyl used in molar proportions with respect to the methacrylonitrile of between 1 and 20%.

18. Solid polymer electrolyte according to Claim 1, characterized in that the methacrylonitrile polymer is a copolymer of methacrylonitrile (MAN) and of at least one (trimethoxysilyl)propyl methacrylate comonomer, the molar proportion of comonomer with respect to the MAN being between 1 and 40%.

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19. Solid polymer electrolyte according to Claim 1, characterized in that the methacrylonitrile polymer is a copolymer of methacrylonitrile (MAN) and of at least one methacrylate comonomer carrying a cyclic carbonate functional group, the molar proportion of comonomer with respect to the MAN being between 1 and 40%.

20. Solid polymer electrolyte according to Claim 1, characterized in that the methacrylonitrile polymer is a copolymer of methacrylonitrile (MAN) and of at least one aromatic olefin chosen from the group consisting of indene, acenaphthylene, vinylnaphthalene, vinylferrocene, vinylpyridine and styrene, which may or may not be substituted, the molar proportion of comonomer with respect to the MAN being between 1 and 30%.

21. Solid polymer electrolyte according to Claim 1, characterized in that the methacrylonitrile polymer is a copolymer of methacrylonitrile (MAN) and of a comonomer of styrene type substituted on the aromatic ring at the meta or para position with respect to the double bond by substituents chosen from  $\text{CH}_3\text{O}$ ,  $\text{CH}_2\text{Cl}$ ,  $\text{CH}_2\text{Br}$ , alkyl radicals having from 1 to 8 carbon atoms and hydroxyalkyl radicals having from 1 to 8 carbon atoms, the molar proportion of comonomer with respect to the MAN being between 1 and 30%.

22. Solid polymer electrolyte according to Claim 1, characterized in that the methacrylonitrile polymer is a copolymer of methacrylonitrile (MAN) and of a comonomer of acrylonitrile, cyanoacrylate or cyanomethacrylate type.

23. Solid polymer electrolyte according to Claim 1, characterized in that the methacrylonitrile polymer is a copolymer of methacrylonitrile (MAN) and of a vinyl comonomer chosen from the group consisting of 1,1-dicyanoethene, vinylimidazole, vinyltriazole, vinyltetrazole, vinyl acetate, vinyl chloride, vinyl fluoride, vinylidene chloride, vinylidene fluoride, vinylene carbonate and maleic anhydride.

24. Solid polymer electrolyte according to Claim 1, characterized in that the methacrylonitrile polymer is

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a diblock or triblock copolymer comprising at least one polymethacrylonitrile sequence and at least one polyether sequence.

25. Solid polymer electrolyte according to  
5 Claim 24, characterized in that the copolymer is a poly(oxyethylene)-block-polymethacrylonitrile (POE-b-MANHP) diblock copolymer.

26. Solid polymer electrolyte according to  
10 Claim 24, characterized in that the copolymer is a poly(oxyethylene)-block-polymethacrylonitrile-block-poly(oxyethylene) triblock copolymer.

27. Polymer electrolyte according to Claim 1,  
15 characterized in that it comprises at least one solvent chosen from propylene carbonate (PC), ethylene carbonate (EC),  $\gamma$ -butyrolactone, dimethoxyethane and dialkyl carbonates.

28. Polymer electrolyte according to Claim 1,  
20 characterized in that it comprises at least one lithium salt chosen from the group consisting of lithium halides, lithium perfluorosulfonate, lithium (trifluoromethylsulfonyl)imide, lithium bis(trifluoromethylsulfonyl)methide, lithium tris(trifluoromethylsulfonyl)methide, lithium perchlorate, lithium hexafluoroarsenate, lithium hexafluorophosphate, lithium  
25 hexafluoroantimonate and lithium tetrafluoroborate.

29. Process for the bulk preparation of a methacrylonitrile polymer by the radical route, characterized in that it comprises the following stages:

30 - a thermal-decomposition free-radical initiator is dissolved in methacrylonitrile or a mixture of methacrylonitrile with at least one comonomer,

35 - the mixture is degassed in order to remove the oxygen and is introduced into a hermetically closed chamber,

- the mixture is brought to a temperature of 60 to 90°C and is maintained at this temperature for 24 to 72 hours.

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30. Process for the preparation of a block copolymer of methacrylonitrile and of ethylene oxide, characterized in that the polymerization of the polymethacrylonitrile block or blocks is carried out by  
5 monofunctional, difunctional or trifunctional anionic initiation from a poly(oxyethylene) block terminated by one, two or three alkoxide groups.

31. Process for the preparation of a block copolymer of methacrylonitrile and of ethylene oxide,  
10 characterized in that the poly(oxyethylene) block or blocks are obtained by mono- or difunctional anionic initiation of the polymerization of ethylene oxide from a living anionic polymethacrylonitrile chain.

32. Process for the preparation of a  
15 methacrylonitrile polymer according to ~~claims 29 to 31~~,  
characterized in that it comprises a crosslinking stage after the polymerization stages.

33. Process for the preparation of a crosslinked or non-crosslinked methacrylonitrile polymer,  
20 characterized in that it comprises a stage of photochemical initiation of radical polymerization by UV radiation which results directly in a thin film of polymer electrolyte.

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